AD-A134 008 THEORETICAL STUDIES IN MOLECULAR FRAGMENTATION: PROCESSES ENERGETICS AND DIAGNOSTICS(U) SMITHSONIAN ASTROPHYSICAL OBSERVATORY CAMBRIDGE MA K P KIRBY 1/1

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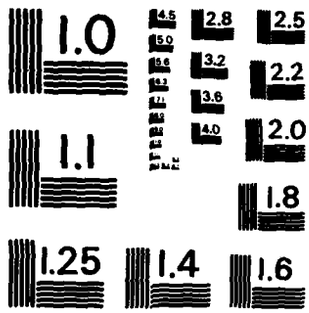

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on the excited electronic states of H_2.

THEORETICAL STUDIES IN MOLECULAR FRAGMENTATION:

PROCESSES, ENERGETICS AND DIAGNOSTICS

Contract N00014-82-K-0536

Annual Report

For the period 1 September 1982 through 31 August 1983

Principal Investigator

Dr. Kate P. Kirby

Prepared for

Office of Naval Research
Arlington, Virginia 22217

September, 1983

Smithsonian Institution
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Cambridge, Massachusetts 02138

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THEORETICAL STUDIES IN MOLECULAR FRAGMENTATION: PROCESSES, ENERGETICS AND DIAGNOSTICS

Annual Progress Report

For the period 1 September 1982 through 31 August 1983

Principal Investigator

Dr. Kate P. Kirby

Our research is directed toward providing diagnostic tools with which to identify and quantify the presence of fragment species and their energy states resulting from molecular destruction processes. The necessary diagnostics data base for small diatomic fragments such as CO, NH, and CN includes potential energy curves, particularly excited electronic states, and transition probabilities. We are using theoretical ab initio methods to calculate the molecular structure and properties of the low-lying $^1\Pi$ and $^1\Sigma^+$ states of CO. In addition, we have used spectroscopic information as well as the theoretical dipole moment of CN, to calculate vibration-rotation transition probabilities and lifetimes for vibrationally hot CN. A postdoctoral research fellow, Dr. Evelyn Goldfield, has been hired, and is currently commencing work on the excited states of NH.

Dr. David L. Cooper and I have recently devised a set of calculations for the $^1\Sigma^+$ and $^1\Pi$ manifolds of CO which appears to be very promising. We construct large-scale configuration interaction (CI) wavefunctions (47,036 and 26,951 configurations for the $^1\Pi$ and $^1\Sigma^+$ states, respectively) which include both valence and Rydberg mixing so that the molecular bonding

regions as well as the atomic asymptotic limits are accurately described. A new set of ALCHEMY programs has been obtained which uses the symbolic matrix method (Liu and Yoshimine, J. Chem. Phys. 74, 612 (1981)), in addition to a direct CI method and has the capabilities needed to obtain efficiently the potential energies for wavefunctions with large numbers of configurations. So far, our calculations give energy splittings in excellent agreement with available spectroscopic data for the known excited $B^1\Sigma^+$ and $E^1\Pi$ states, both of which have some Rydberg character at small internuclear separations R, and at large R dissociate to ground state atoms. We anticipate that we will also be able to characterize the new $D^1\Sigma^+$ state which has recently been identified from laser-induced fluorescence studies (G.L. Wolk and J.W. Rich, J. Chem. Phys. 79, 12 (1983)). The transition moments obtained from our preliminary calculations on the $X^1\Sigma^+ - A^1\Pi$ system have been shown to be in excellent agreement with experimental measurements (R.W. Field et al., J. Chem. Phys. 78, 2838 (1983)).

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